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Mössbauer spectroscopic studies of frozen aqueous solutions of Fe^{3+} salts

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Frozen aqueous solutions (FAS) of Fe^{3+} salts have been investigated by use of Mössbauer spectroscopy in order to study the conditions for formation of glasses. A general discussion of spin–spin relaxation in glasses is given, and we discuss how changes in the spin–spin relaxation time can be attributed to changes in the average separation between the iron ions. In the $FeCl_3$–H_2O system, it was found that homogeneous glasses are easily formed when the salt concentration is larger than 3.5 moles $FeCl_3$ per 100 moles H_2O. In more dilute samples, ice crystallizes during cooling, while the salt concentration of the solution increases. At low temperatures the crystallization terminates and the remaining liquid solidifies into a glass. During exposure at 200 K, the dilute samples change irreversibly. This is discussed in terms of a metastable phase diagram. The properties of frozen solutions with other glass forming agents such as NO_3^-, ClO_4^-, and glycerol are also discussed. In some systems it was found that the states obtained after cooling depend critically on the cooling rate.

I. INTRODUCTION

Mössbauer spectroscopy has been extensively used for the investigation of frozen aqueous solutions (FAS).[1–18] When an aqueous solution is cooled, it may crystallize in phases of specific compositions. However, under certain conditions crystallization does not take place, and a vitreous state of the same composition and probably of similar structure as the solution is formed. If the FAS contain suitable isotopes, the various phases can be studied by means of Mössbauer spectroscopy.

Most of the previous Mössbauer work on FAS has been performed with salts of divalent iron. Mössbauer spectra of Fe^{2+} complexes normally show double line spectra with large quadrupole splittings, the sizes of which depend on the crystal field at the iron site. Therefore, studies of FAS of Fe^{2+} salts give information on the coordination to the nearest neighbors.

Contrary to Fe^{2+} Mössbauer spectra, Fe^{3+} spectra of FAS often show paramagnetic hyperfine splitting (hfs) due to the magnetic interaction between the nucleus and the electronic spin. However, the spectra are often affected by relaxation of the electronic spin among the ionic levels.

The Mössbauer spectra depend strongly on the electronic relaxation time τ when τ is comparable with the nuclear Larmor period. For $\tau \gtrsim 25$ ns, resolved magnetic hyperfine split spectra can be found with a linewidth decreasing with increasing τ. In the range 1 ns $\lesssim \tau \lesssim$ 25 ns, the splitting is blurred, and identification of individual lines is not always possible. In the fast region, $\tau \lesssim 1$ ns, the magnetic hyperfine splitting collapses to one line or two, with linewidth decreasing with decreasing τ. Essentially Lorentzian line shapes of natural width are found for $\tau < 0.01$ ns and $\tau > 100$ ns.

The rate of electronic transitions, $\tau^{-1} = \tau_{sl}^{-1} + \tau_{ss}^{-1}$, is determined by two mechanisms: (1) the spin–lattice relaxation with transition rate τ_{sl}^{-1} and (2) the spin–spin relaxation with transition rate τ_{ss}^{-1}.

The ^6S ground state of the Fe^{3+} ion is spherically symmetric. Therefore, the coupling between the lattice and the spin of the ion is weak. This favors a long spin–lattice relaxation time τ_{sl}. For temperatures well below the Debye temperature Θ_D, $\tau_{sl} \propto T^{-7}$, but for $T \gg \Theta_D$, $\tau_{sl} \propto T^{-2}$.[19]

The spin–spin relaxation is due to the magnetic dipole interaction and exchange interaction between the magnetic ions. τ_{ss} is essentially independent of temperature, but increases with increasing dilution of magnetic ions.

If the average spacing between the Fe^{3+} ions is larger than about 15 Å, corresponding to an ion concentration of about 0.5 mole/liter, the spin–spin relaxation is so slow that well-resolved magnetically hyperfine split spectra can be observed at low temperatures. The line positions depend on the immediate surroundings of the Fe^{3+} ions. If the ion concentration is increased, τ_{ss} decreases, and the hyperfine split spectra may collapse to one line or two, with a width that gives information on the average spacing between the Fe^{3+} ions. This feature of Fe^{3+} Mössbauer spectra is valuable in the study of FAS.[14,15]

If a glass is formed during the cooling of an aqueous solution of a ferric salt, the iron ions may be distributed at random. However, if crystallization of ice takes place during cooling, the iron ions are mainly found in regions of higher concentration, because the solubility of iron ions in ice is very low. The main purpose of this work was to study the conditions for glass formation during freezing of aqueous solutions of Fe^{3+} salts.

II. EXPERIMENTS

The solutions were prepared by dissolving weighed amounts of $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, or $Fe(ClO_4)_3 \cdot 9H_2O$ (and when desired a glass forming agent) in distilled water. The solutions were injected into a container, consisting of a short copper tube closed with thin Mylar foils glued on to the ends. The thickness was 1, 2, or 3 mm. The copper was protected against chemical reaction with the solutions by a thin layer of araldit epoxy. These containers allow a rapid cooling and visual inspection of the absorber material after freezing. The absorbers were frozen immediately after preparation of the solutions by immersion into liquid nitrogen. The

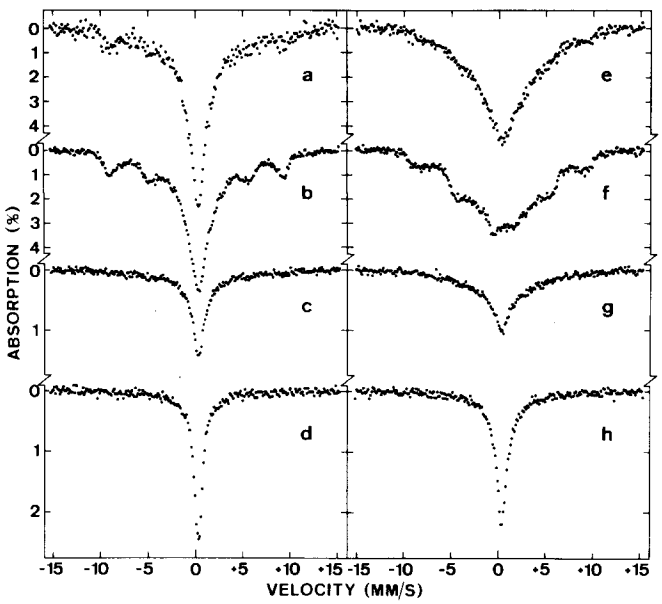

FIG. 1. Mössbauer spectra obtained at 80 K of FAS of $FeCl_3$ at various concentrations x. a: $x=4.5$, b: $x=3.5$, c: $x=0.5$, d: $x=0.5$, but after exposure at 200 K for 1 h. a, b, c, and d were obtained in an applied field of 50 Oe. e, f, g, and h are spectra of the same absorbers in an applied field of 12.4 kOe.

violent boiling ceased, indicating thermal equilibrium, after a freezing time t, of 5–15 s depending on the absorber thickness. The absorbers were attached in a cold cryostat and were in no case heated to more than about 120 K during the mounting.

The Mössbauer spectra were obtained in transmission geometry with spectrometers of the conventional constant acceleration type. Sources of ^{57}Co in Pd were used giving a linewidth of about 0.23 mm/s with a thin absorber of metallic iron.

External magnetic fields up to 12.4 kOe were applied perpendicularly to the gamma ray direction by use of an electromagnet with iron pole shoes. The acidity of the solutions (pH) was measured using a commercial pH meter with glass and calomel electrodes.

III. RESULTS

A. $FeCl_3 + H_2O$

In order to investigate basic features of the glassy and crystalline states of a FAS, one system was studied extensively, namely $FeCl_3 + H_2O$. Figure 1 shows some typical spectra of absorbers with various concentrations, x, given in moles $FeCl_3$ per 100 moles H_2O. The absorber thickness was 2 mm and the freezing time $t \simeq 10$ s. The spectra were obtained at 80 K in external fields of 12.4 kOe and in the remanent field, which was about 50 Oe. Most of the obtained spectra consist essentially of a single line, broadened by electronic relaxation. In some cases side lines can be seen, indicating a partly resolved magnetic hfs, but in all cases the relaxation time is so short that the width of the spectrum, Γ (full-width at half-maximum), can be used as a rough measure of the relaxation time.

Figure 2 shows the phase diagram of $FeCl_3 + H_2O$[20,21] and the Mössbauer linewidth at 80 K as a function of the concentration x. Results are given for applied fields of 50 Oe and 12.4 kOe before and after heat treatment of the absorbers at 200 K for 1 h. In the phase diagram we have omitted the crystalline phase $FeCl_3 \cdot 10H_2O$, because this phase is very unlikely to crystallize, unless special effort is made.[22]

It can be seen that the Mössbauer linewidth (and the relaxation time) of the absorbers before heat treatment exhibits a pronounced maximum for $x \simeq 3.5$. By visual inspection it was found that the absorbers with $x \geq 3.5$ were transparent with some cracks, indicating that a glassy state was formed. However, the less concentrated absorbers were opaque and seemed to consist of a large number of small crystals. Exposure of the absorbers with $x < 5.5$ at 200 K for 1 h resulted in an irreversible line narrowing, whereas the more concentrated absorbers were unaffected by this treatment.

Absorbers with $x = 3.25$ were frozen at various freez-

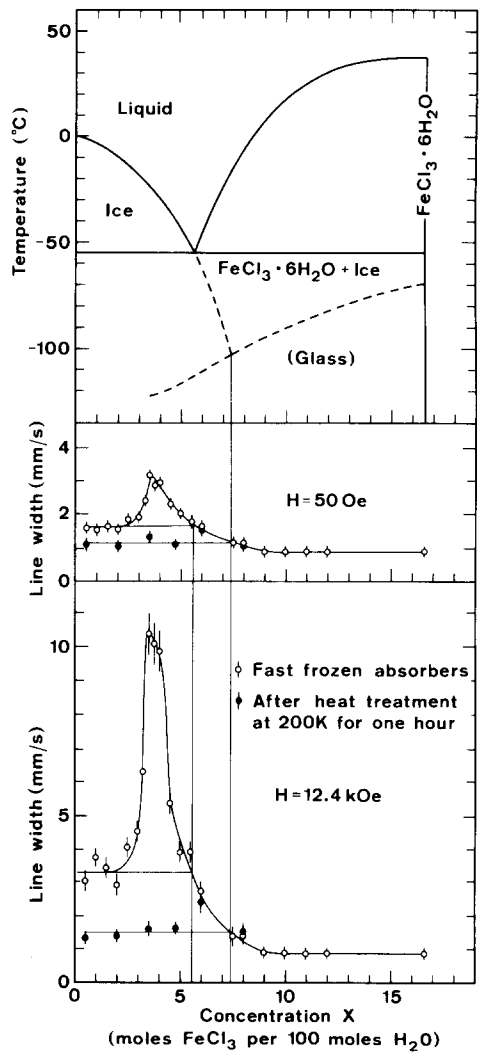

FIG. 2. The upper part of the figure shows the phase diagram of the $FeCl_3$–H_2O system. The dotted lines indicate the metastable phase diagram including the extrapolated hypoeutectic liquidus curve and the glass curve. In the lower part of the figure is shown the Mössbauer linewidth (FWHM) of FAS of $FeCl_3$ at 80 K at applied fields of 50 Oe and 12.4 kOe as a function of the concentration.

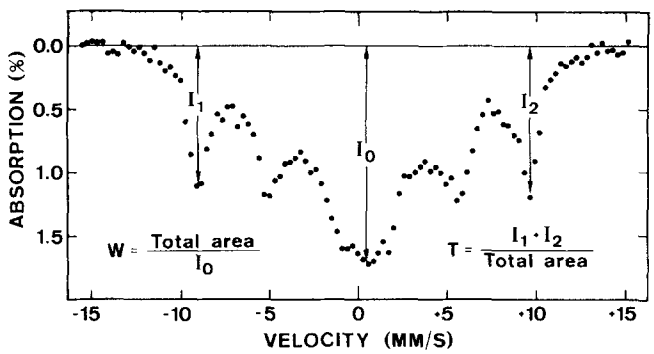

FIG. 3. Mössbauer spectrum obtained at 78 K in zero applied field of a FAS of 0.5M $Fe(NO_3)_3$ and 2.0M HNO_3 with 33% glycerol added as a glass former. The definitions of the parameters W and T are indicated.

ing rates by changing the absorber thickness. One absorber, frozen in 4.5 s, was transparent and showed a broad spectrum with well-developed side lines, whereas another absorber, frozen in 13 s, was opaque and showed a narrower spectrum. Thus a close connection between the state of the absorber and its Mössbauer line shape generally seems to exist.

Some absorbers with different iron concentration were also studied at temperatures above 80 K and at 4.5 K. Significant changes were only found at temperatures above 120 K. It was found that the linewidth decreases with increasing temperature and the magnetic hfs, seen in some cases at 80 K, disappears at higher temperatures.

An analysis of the temperature dependence of the area of the Mössbauer spectra of the absorbers with $x = 2.0$, $x = 3.5$, $x = 4.75$, and $x = 6.0$ showed that the Debye temperature, Θ_D, equals 235 ± 20 K.

B. $Fe(NO_3)_3$ + glass formers

A number of acid aqueous solutions ($pH \leq 0$) were prepared with a constant volume concentration of iron (0.5M, i.e., 0.5 moles Fe^{3+}/liter; this concentration is comparable with that of $FeCl_3$ solutions with $x \simeq 1.0$ mole Fe/100 moles H_2O). Absorbers were frozen under identical conditions (freezing time $t \simeq 12$ s) but with different glass forming agents added. The Mössbauer spectra were obtained at 78 K without applied magnetic field.

The connection between the visual appearance of the absorbers and their Mössbauer spectra was again obvious. All absorbers with a glassy appearance had similar spectra with resolved hfs ($H_{eff} \simeq 580$ kOe, $\delta_{Fe} \simeq 0.5$ mm/s). The opaque absorbers showed broad, essentially single line spectra, but occasionally with indication of poorly resolved hfs.

As a rough measure of the partial resolution of the magnetic hfs we use the parameters W and T, defined in Fig. 3.

Of all glasses investigated, those frozen with glycerol gave spectra with the best resolved hfs at 78 K, whereas the highly ionic glasses, like those frozen with $LiNO_3$, gave the least resolved hfs. A similar difference was found at 4.5 K. The parameters W and T of the spectra are given in Table I.

The line positions were identical in the spectra of absorbers with the two glass formers (frozen immediately after the preparation of the solutions). Measurements with absorbers enriched in ^{57}Fe {which allows more dilute samples [$\simeq 0.02M$ $Fe(NO_3)_3$] and therefore gives better resolved hfs}, frozen with glycerol or $LiNO_3$ as glass formers also showed identical line positions. This indicates that the inner coordination sphere of the Fe^{3+} ions is independent of the glass former used.

In order to study the role of the amount of added glass former we prepared a series of FAS with a concentration of 0.5M $Fe(NO_3)_3$ and 2.0M HNO_3, but with different molar concentrations, c, of $NaNO_3$, $0 \leq c \leq 4.5M$. Some

TABLE I. Hyperfine resolution W and T of the Mössbauer spectra of some glasses.

Composition of aqueous solution			Resolution of hfs	
Salt	Acid	Glass former	W (cm/s)	T (s/cm)
0.5M $Fe(NO_3)_3$	2.0M HNO_3	33% Glycerol	1.24 ± 0.03[a]	1.06 ± 0.03[a]
0.5M $Fe(NO_3)_3$	2.0M HNO_3	60% Glycerol	1.26 ± 0.03[a]	1.00 ± 0.02[a]
0.5M $Fe(NO_3)_3$	2.0M HNO_3	33%Methanol	1.18 ± 0.03[a]	0.90 ± 0.03[a]
0.5M $Fe(NO_3)_3$	2.0M HNO_3	3.0M $NaNO_3$	1.16 ± 0.02[a]	0.96 ± 0.03[a]
0.5M $Fe(NO_3)_3$	2.0M HNO_3	4.5M $NaNO_3$	1.19 ± 0.03[a]	0.98 ± 0.03[a]
0.5M $Fe(ClO_4)_3$	2.0M $HClO_4$	1.0M $NaClO_4$	1.14 ± 0.04[a]	0.80 ± 0.05[a]
0.5M $Fe(ClO_4)_3$	2.0M $HClO_4$	3.0M $NaClO_4$	1.10 ± 0.05[a]	0.80 ± 0.05[a]
0.5M $Fe(NO_3)_3$	0.5M HNO_3	4.5M $LiNO_3$	1.08 ± 0.02[a]	0.87 ± 0.03[a]
0.5M $Fe(NO_3)_3$	0.5M HNO_3	4.5M $LiNO_3$		0.78 ± 0.03[b]
0.5M $Fe(NO_3)_3$	0.5M HNO_3	4.5M $LiNO_3$		1.17 ± 0.02[c]
0.5M $Fe(NO_3)_3$	0.5M HNO_3	40% Glycerol		1.01 ± 0.02[b]
0.5M $Fe(NO_3)_3$	0.5M HNO_3	40% Glycerol		1.44 ± 0.03[c]

[a]Spectrum obtained at 78 K without applied magnetic field.
[b]Spectrum obtained at 78 K in applied magnetic field of 400 Oe.
[c]Spectrum obtained at 4.5 K in applied magnetic field of 400 Oe.

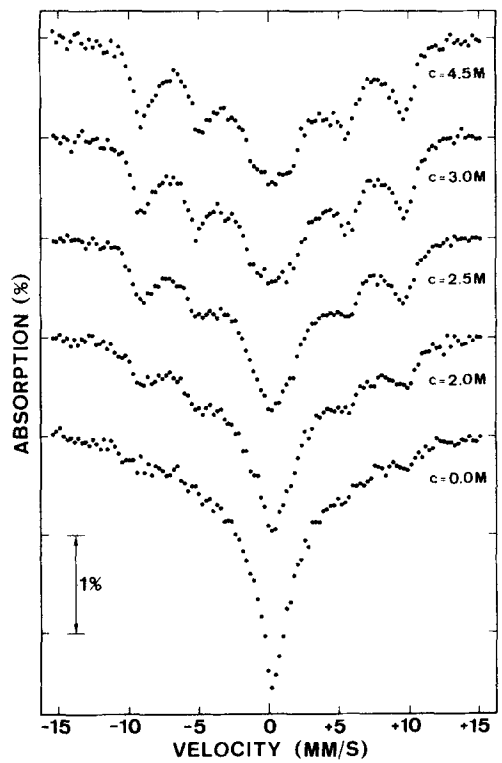

FIG. 4. Mössbauer spectra of FAS of 0.5M $Fe(NO_3)_3$, 2M HNO_3, and various concentrations c of $NaNO_3$. The spectra were obtained at 78 K in zero applied field.

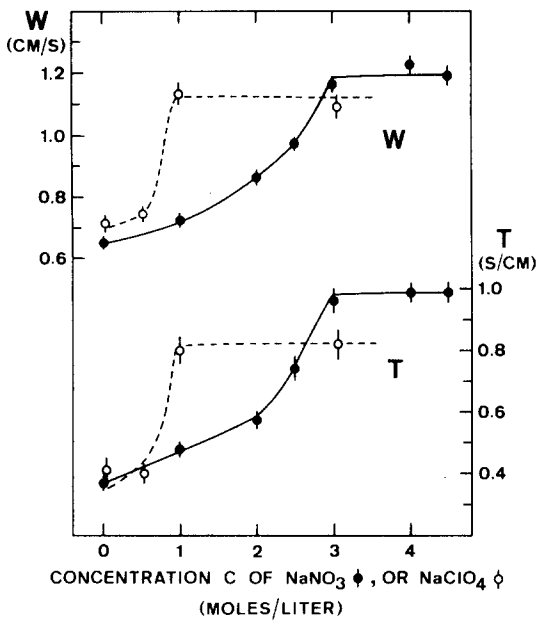

FIG. 5. Hyperfine resolution parameters W and T of FAS of composition 0.5M $Fe(NO_3)_3$, 2.0M HNO_3, c M $NaNO_3$ and 0.5M $Fe(ClO_4)_3$, 2.0M $HClO_4$, c M $NaClO_4$. The spectra were obtained at 78 K in zero applied field.

of the Mössbauer spectra are shown in Fig. 4.

The FAS with $c \geq 3.0M$ all had a glassy appearance, and their spectra were identical, showing a partly resolved hfs. The absorber with $c = 2.5M$ had an opaque central part, surrounded by a glassy rim. All the absorbers with $c \leq 2.0M$ were opaque, and their spectra show decreasing resolution of the hfs with decreasing c. With the given freezing time $t \simeq 12$ s there seems to be a critical concentration $c \simeq 3.0M$ of $NaNO_3$ for the glass formation.

Investigation of FAS of 0.5M $Fe(ClO_4)_3$, 2.0M $HClO_4$, and various concentrations c of $NaClO_4$ gave similar results, except that the critical concentration of $NaClO_4$ for glass formation was $c \simeq 1.0M$. The parameters W and T of the spectra obtained with the two glass formers are shown in Fig. 5.

The role of the freezing conditions was studied by preparing a number of absorbers of identical composition [namely, the critical one, 0.5M $Fe(NO_3)_3$, 2.0M HNO_3, and 3.0M $NaNO_3$]. The absorbers were frozen at various freezing rates by changing the thermal contact to the liquid nitrogen bath. During the cooling the temperature was measured with a thermocouple inside the absorber (except for the fastest rate $\simeq$ 5000 K/min, which was obtained by dipping into liquid nitrogen pieces of filter paper made wet by the solution). The freezing rate r was defined as the average rate in the temperature range 273 K–125 K. The parameters W and T of the Mössbauer spectra are shown in Fig. 6.

It can be seen that there exists a critical rate, $r = r_0$, 220 K/min $< r_0 <$ 570 K/min. The quickly frozen absorbers ($r > r_0$) had a glassy appearance and showed identical Mössbauer spectra, whereas the slowly frozen absorbers ($r < r_0$) were opaque and showed identical spectra with less resolved magnetic hfs.

IV. DISCUSSION

A. Iron complexes

The Mössbauer spectra of FAS may give information about the iron complexes present. The amounts of various complexes in glasses may be similar to those found in the liquid of which the glasses are frozen. However, the equilibrium constants measured at room temperature cannot be expected to give correct results for FAS.

The Mössbauer spectra of glasses with NO_3^-, ClO_4^-, or glycerol were essentially identical when the iron concentration was kept constant. The Fe^{3+} ions therefore seem to form identical complexes in these samples. Absorbers with low iron concentration showed a magnetic hfs corresponding to a maximum hyperfine field of 580 kOe. The iron complex present in these absorbers is probably $[Fe(H_2O)_6]^{3+}$.

Dilute absorbers containing $FeCl_3$ and with glycerol added as a glass former showed a smaller magnetic hfs corresponding to a maximum hyperfine field of about 560 kOe. Spectra of the concentrated absorbers with $x > 9$, in which relaxation is fast, show a quadrupole splitting, $\Delta = 0.39 \pm 0.02$ mm/s. It has been suggested[23] that a complex of the type $[FeCl_2(H_2O)_4]^+$ similar to that found in crystalline $FeCl_3 \cdot 6H_2O$ is predominant in the aqueous solutions of $FeCl_3$. Spectra of a glassy and a crystalline absorber of the composition $FeCl_3 \cdot 6H_2O$ are shown in Fig. 7. Both spectra show an isomer shift $\delta_{Fe} = 0.53$ mm/s. However, the quadrupole splitting of crystalline $FeCl_3 \cdot 6H_2O$ ($\Delta = 0.89 \pm 0.02$ mm/s) exceeds that found in the concentrated FAS of $FeCl_3$ by more than a factor of 2. It is therefore unlikely that the Fe^{3+} ions

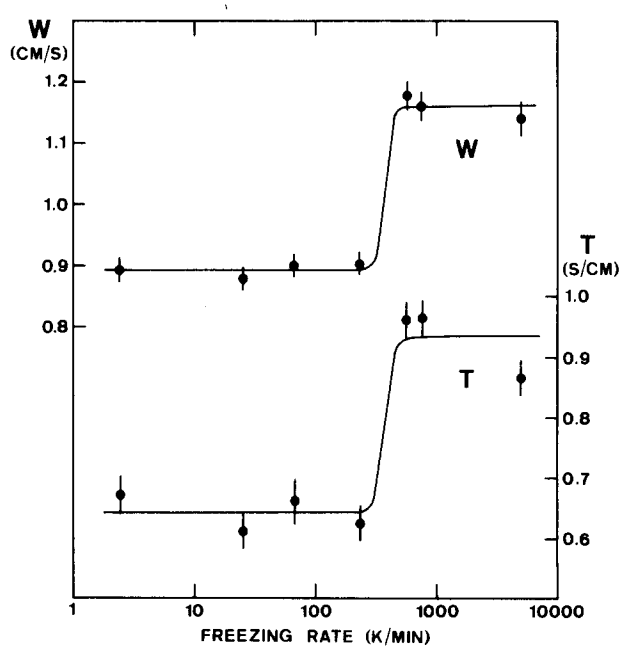

FIG. 6. Hyperfine resolution parameters W and T of FAS of 0.5M $Fe(NO_3)_3$, 2.0M HNO_3, 3.0M $NaNO_3$ as a function of the freezing rate. The spectra were obtained at 78 K in zero applied field.

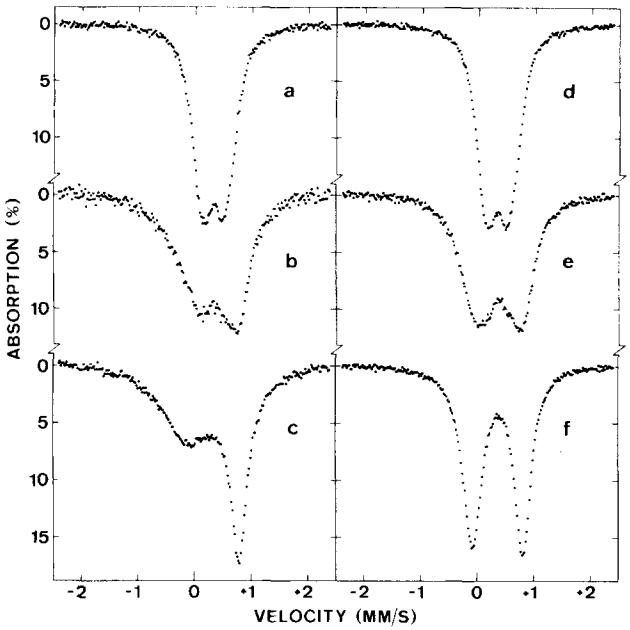

FIG. 7. Mössbauer spectra obtained at 80 K of absorbers of the composition $FeCl_3 \cdot 6H_2O$. a: glassy absorber, fast frozen from the melt. b: after exposure of the absorber at 273 K for several hours. c: spectrum of crystalline $FeCl_3 \cdot 6H_2O$. a, b, and c were obtained in an applied field of 50 Oe. d, e, and f are spectra of the same absorbers in an applied field of 12.4 kOe.

have similar nearest neighbor configurations in the two systems.

In crystalline $FeCl_3 \cdot 6H_2O$ the iron is octahedrally coordinated to four H_2O molecules with two Cl^- ions in the *trans* positions.[24] In FAS the two Cl^- ions may be coordinated to the iron in *cis* positions. If only nearest neighbor interaction is important the quadrupole splitting would decrease by a factor of about 2. However, we cannot exclude the possibility that the iron ions are coordinated to only one or to three Cl^- ions.

B. Spin-lattice relaxation

When the relaxation broadening of the Mössbauer spectra is used to obtain information on the properties of the absorber material, it is important to know the relative importance of spin–spin relaxation and spin–lattice relaxation. The influence of spin–lattice relaxation can be found from the temperature dependence of the relaxation time. The constant linewidth of FAS of $FeCl_3$ at temperatures below 120 K demonstrates that the relaxation time is essentially independent of temperature. As the spin–lattice relaxation time τ_{sl} decreases with increasing temperature it can be concluded that τ_{sl} is long compared with the spin–spin relaxation time τ_{ss} in these absorbers at 80 K. The dependence of the linewidth on the concentration and the applied magnetic field can therefore be attributed to changes in the spin–spin relaxation time.

In more dilute absorbers, where the spin–spin relaxation time is longer, it is possible to see the influence of spin–lattice relaxation at 80 K. An example of this is given in Table I. The absorbers with 0.5*M* $Fe(NO_3)_3$, 0.5*M* HNO_3 and with $LiNO_3$ or glycerol added as glass formers show a significant difference between the resolution of the hfs of the spectra obtained at 4.5 K and those obtained at 78 K. In the absorbers studied here, we found that $\tau_{sl} \simeq 25$ ns at 78 K. When the relaxation time is shorter, it must therefore be due to fast spin–spin relaxation, and for $\tau \lesssim 5$ ns the influence of spin–lattice relaxation is negligible.

C. Spin-spin relaxation

The spin Hamiltonian of the Fe^{3+} ion may be written

$$H = H_{cf} + H_Z + H_{dd} + H_{ex} + H_{hf} .$$

The terms represent the crystal field interaction, the electronic Zeeman interaction due to an external magnetic field, the magnetic dipole–dipole and exchange interactions with the neighboring ions, and the hyperfine interaction, respectively.

In magnetically dilute systems, H_{ex} is supposed to be negligible. Furthermore, H_{hf} is normally small compared with the other terms. In the following we assume that the dominating terms of H are $H_{cf} + H_Z = H_0$. Then H_{dd} may be considered as a perturbation which broadens the energy levels E_0 of H_0 and gives rise to transitions among the eigenstates $|E_0\rangle$ (spin–spin relaxation).

The most probable spin–spin relaxation process consists in simultaneous transitions among the eigenstates of two neighboring ions.[17,25] Bloembergen *et al.*[26] have given an expression for the probability per unit time for a process which results in an increase in the Zeeman and crystal field energy of an ion i by an amount E_α and a decrease in energy of another ion j by an amount E_β. The energy difference $E_\alpha - E_\beta$ is taken up by the magnetic interaction energy of the whole spin system. If the shape functions of the transitions E_α and E_β are Gaussian with second order moments $(\Delta E_\alpha)^2$ and $(\Delta E_\beta)^2$, the expression for the transition probability is written

$$\begin{aligned} W_{ij}(\alpha,\beta) &= (2\pi)^{1/2} h^{-1} |H_{ij}|^2 [(\Delta E_\alpha)^2 + (\Delta E_\beta)^2]^{-1/2} \\ &\quad \times \exp\{-(E_\alpha - E_\beta)^2 / 2[(\Delta E_\alpha)^2 + (\Delta E_\beta)^2]\} \\ &= w_{ij}(\alpha,\beta) \exp[-\delta_{ij}(\alpha,\beta)] , \end{aligned} \tag{1}$$

where

$$|H_{ij}|^2 = |\langle E_a^{(i)}, E_b^{(j)} | H_{ij} | E_a^{(i)} + E_\alpha, E_b^{(j)} - E_\beta \rangle|^2 .$$

H_{ij} is the Hamiltonian of the magnetic interaction between the ions i and j, $\sum_j H_{ij} = H_{dd}$. $|E_a^{(i)}\rangle$ and $|E_b^{(j)}\rangle$ are the initial states of the ions i and j.

The assumption of a Gaussian shape is not correct in the presence of strong exchange interaction[27] or for random magnetic dilution.[28] Equation (1) should therefore be considered to be only a first approximation to the real transition probability in glasses.

The spin–spin relaxation time of the ion i in the state $|E_a\rangle$ may be defined by

$$(\tau_{ss}^{(i)})^{-1} = \sum_{j,b,\alpha,\beta} W_{ij}(\alpha,\beta) p_j(b) , \tag{2}$$

where $p_j(b)$ is the probability for the ion j to be in the state $|E_b\rangle$.

It is not straightforward to find the concentration dependence of the spin–spin relaxation time in glasses. It must be realized that each ion in a glass has its unique surroundings of magnetic ions. Therefore, the relaxation times of different ions are not identical. Furthermore, the way in which the distances change when the concentration varies may not be described by a simple model. One could imagine that the dilution could be described as a removal of the fraction $1-f$ of magnetic ions, while the remaining fraction f still occupies the original positions. As the second order moment $(\Delta E)^2$ is proportional to the mean square value of the local magnetic dipole field, it can be shown that $(\Delta E)^2$ is reduced by a factor f.[28] In addition, on the right-hand side of Eq. (2) the summation over j must be replaced by a summation over the remaining fraction f of ions, j'. We then find an approximate expression for the relaxation time:

$$[\tau_{ss}^{(i)}(f)]^{-1} = \sum_{j',b,\alpha,\beta} W_{ij'}(\alpha,\beta) p_{j'}(b)$$

$$= f^{1/2} \sum_{j,b,\alpha,\beta} w_{ij}(\alpha,\beta) \exp[-\delta_{ij}(\alpha,\beta)/f] p_j(b) . \tag{3}$$

In a glass the nearest surroundings of two Fe^{3+} ions may be identical and may therefore have the same crystal field splittings. However, the orientations of the crystal field axes generally differ. When a magnetic field H is applied the energy splitting depends on the angle between the crystal field axes and the field direction. Consequently, the transition energies E_α and E_β may be equal for equivalent transitions of two ions, when $H=0$, but different for $H \neq 0$.[17,25] This implies that for $H=0$ the exponential factors of Eqs. (1) and (3) may be replaced by unity. Other transitions with $E_\alpha \neq E_\beta$ have a much lower probability and are therefore unimportant. According to Eq. (3), we find for $H=0$

$$\tau_{ss}^{(i)}(f) = \tau_{ss}^{(i)}(f=1) f^{-1/2} .$$

If an external magnetic field is applied, we have that generally $E_\alpha \neq E_\beta$ for all transitions of two neighboring ions. According to Eq. (3), this implies that the concentration dependence of τ_{ss} is considerably enhanced by the exponential factor.

It must be emphasized that these results may only be correct if the model used for dilution is reasonable, and if the shape functions for the transitions E_α and E_β are Gaussian. Furthermore, we have here considered only the double spin flip processes. Single spin flip processes may be important at low fields, where the Zeeman splitting of a Kramers doublet is comparable to the linewidths.

The difference in concentration dependence for small and large applied fields is demonstrated in Fig. 2 for $3.5 < x < 6.0$. In this concentration range, the fast frozen absorbers are glasses and the Mössbauer spectra are influenced by relaxation. The concentration dependence of the linewidth (and consequently the concentration dependence of the relaxation time) is much more pronounced for $H = 12.4$ kOe than for $H = 50$ Oe.

D. Glass formation

Freezing of an aqueous solution may result in the formation of various states depending on the cooling rate and the initial composition. The thermodynamic stable state below the liquidus temperature T_l is crystalline. This state is obtained only if the cooling rate is low enough to allow both nucleation of microcrystals and subsequent crystal growth. Fast cooling may prevent crystallization and may thus result in the formation of a metastable vitreous state below the glass temperature T_g. The glass temperature depends on the composition and may be defined as the temperature where the viscosity $\eta \simeq 10^{14}$ P.

The temperature dependence of the nucleation rate I in the supercooled liquid may be written[29,30]

$$I \alpha \exp[-(F^* + Q)/kT] .$$

Here Q is an activation energy for short range diffusion and atomic rearrangements and F^* is the free energy barrier which must be surmounted when a new liquid–solid interface is created. The barrier F^* is to a good approximation proportional to $(T_l - T)^{-2}$ where $T_l - T$ is the supercooling.

Just below the liquidus temperature T_l, the nucleation rate increases with the supercooling, but at low temperatures the influence of the activation energy Q is dominating and causes a rapid decrease in nucleation rate.

The rate of crystal growth is often assumed to be proportional to $(T_l - T)/\eta$.[29,30] η is the viscosity of the supercooled liquid and it depends exponentially on the reciprocal temperature. Hence the crystal growth rate, like the nucleation rate, increases with the supercooling, has a maximum at a certain temperature, and approaches zero at further cooling due to the exponential temperature dependence of the transport properties of the liquid.

When pure water is cooled by conventional methods to sufficiently low temperatures, it always crystallizes into ice. However, if for example a salt is dissolved in water, or if a suitable alcohol is added, the freezing point is lowered, and this may cause a decrease in the rates of nucleation and crystal growth at a given supercooling. Hence the solution may solidify into a glass at ordinary cooling rates.

The results of the experiments with the $FeCl_3$–H_2O system may be understood with reference to the phase diagram shown in Fig. 2. The fast frozen absorbers with $x \geq 3.5$ all had a glassy appearance and the linewidth follows at least qualitatively the expected dependence on the iron concentration, which is discussed in Sec. IV. C. These absorbers therefore seem to be homogeneous glasses. None of the spectra of these absorbers showed any trace of the spectrum of crystalline $FeCl_3 \cdot 6H_2O$, shown in Fig. 7. The fast frozen absorber with stoichiometric composition ($x = 16.66$) did not crystallize when kept at 200 K or 240 K for 1 h. Only during heating to 273 K for several hours did it show partial crystallization as shown in Fig. 7. Thus the crystallization rate of $FeCl_3 \cdot 6H_2O$ seems to be very low.

The dilute absorbers ($x < 3.0$) did not solidify as homogeneous glasses when cooled rapidly ($t \simeq 10$ s). These absorbers were opaque. This indicates that crystallization takes place during cooling. However, when these absorbers were heated to 200 K and kept at this temperature for 1 h and then recooled to 78 K, the Mössbauer spectra changed irreversibly. Behavior of this kind is often found in glasses. Before heating, all these absorbers showed identical Mössbauer linewidths, namely about 1.6 mm/s at $H = 50$ Oe, and 3.3 mm/s at $H = 12.4$ kOe. It may therefore be concluded that the iron ions are located in glassy regions with a composition which is independent of the initial concentration of the solution. Similar results have been found in studies of FAS of $Fe(ClO_4)_3$[16] and in other systems.[31]

If we compare the observed linewidths of the dilute and glassy absorbers, we find that the linewidths of the dilute absorbers both at 50 Oe and at 12.4 kOe are equal to that of a homogeneous glass with an iron concentration $x \simeq 5.5$.

On the basis of these observations we may draw some conclusions about the kinetics of the freezing process. When a sample of an initial concentration $x < 3.0$ is frozen, nucleation and growth of ice crystals initiate at a certain supercooling. As the temperature is decreased, the crystal growth continues, while the iron concentration in the liquid increases following a curve below the hypoeutectic liquidus curve of the equilibrium phase diagram. The detailed relation between temperature and composition of the liquid depends on the freezing rate. At a certain temperature T_0 and a certain composition of the liquid x_0, the crystal growth rate becomes slow compared with the cooling rate, and eventually the solution solidifies into a glass with $x \simeq x_0$. Samples with different initial concentrations will only differ with respect to the amount of ice when cooled to a temperature slightly above T_0, but not with respect to the composition of the liquid. This explains why samples in which ice crystallizes during cooling all have the same iron concentration of the glass when cooled at the same cooling rate. The local iron concentration of the absorbers frozen in about 10 s is $x_0 \simeq 5.5$, which is close to the eutectic composition, but we believe that this is accidental.

The reason for formation of a homogeneous glass in the region $3.5 < x < 5.5$ cannot be a too small crystal growth rate. A small growth rate would imply that the final local concentration of iron in the absorbers with $x < 3.0$ should be $x \simeq 3.5$. Therefore, the reason must be a too slow nucleation rate of ice crystals favored by the lowering of the liquidus temperature with increasing concentration of $FeCl_3$.

After heat treatment for 1 h at 200 K (which is above the glass temperature T_g) and recooling to 80 K, all the absorbers with $x < 5.0$ showed spectra with a linewidth that had decreased to $\Gamma \simeq 1.2$ mm/s for $H = 50$ Oe and $\Gamma \simeq 1.5$ mm/s for $H = 12.4$ kOe. This corresponds to a local iron concentration $x \simeq 7.3$. Furthermore, we observed that the absorbers with $3.5 < x < 5.0$, which initially were glassy, became opaque during the heat treatment. We therefore conclude that both nucleation and growth of ice crystals do take place at 200 K when sufficient time is available.

As $FeCl_3 \cdot 6H_2O$ does not crystallize the state of the dilute absorbers at 200 K may be found from the extrapolated liquidus curve shown in Fig. 2. When the samples are recooled slowly (cooling time for cooling to 80 K was about 30 min), growth of ice crystal may take place, while the concentration of the liquid follows the extrapolated liquidus curve. During slow cooling, the crystal growth terminates at a certain temperature that may be close to the glass temperature of the liquid. In fact, it is seen in Fig. 2 that the local concentration $x \simeq 7.3$ of the heated absorbers is close to the concentration at the intersection of the extrapolated liquidus curve and the glass curve.

The results of the experiments with other glass formers shown in Fig. 5 may also be interpreted in terms of a change in nucleation rate with the salt concentration. In the solutions with salt concentrations $c > 3.0M$ $NaNO_3$ or $c > 1.0M$ $NaClO_4$, respectively, nucleation does not take place during the freezing ($t = 12$ s). In more dilute solutions, nucleation and growth of ice occurs. As in FAS of $FeCl_3$, crystallization terminates at a low temperature, and the remaining solution solidifies into a glass. However, as shown in Fig. 5, the local iron concentration in the fast frozen solutions of the multicompound system increases with decreasing initial salt concentration. This may be due to a displacement of the equilibrium between ice and solution as the relative amounts of the nonaqueous components are changed.

The dependence of the final state on the freezing rate shown in Fig. 6 indicates that nucleation of ice does occur for cooling rates smaller than 220 K/min. In this case the amount of ice seems to be independent of the cooling rate over two decades. Hence we conclude that the decrease in crystal growth rate at low temperatures is rather steep. This is in agreement with the expected exponential behavior of the transport properties at low temperatures.[29,30]

The Mössbauer parameters given in Table I of glassy absorbers frozen with different glass formers indicate that the Fe^{3+} ions are distributed in nearly the same way in these absorbers. However, small differences are found between glasses frozen with glycerol and those frozen with $LiNO_3$. The departures found at 80 K may be explained in terms of a difference in spin–lattice relaxation time. But departures are also found at 4.5 K, where only spin–spin relaxation influences the spectra. The faster relaxation in the $LiNO_3$ glass may therefore be attributed to an inhomogeneous distribution of iron ions. This may be due to a phase separation in the supercooled solution in two immiscible liquids of different iron concentration, as discussed by other authors.[21,32]

V. CONCLUSIONS

Mössbauer spectroscopic studies of FAS of ferric salts elucidate several properties of the samples. In most cases, spin–lattice relaxation plays a minor role compared with spin–spin relaxation at temperatures

below 120 K. Therefore, observed changes in relaxation time can be attributed to changes in spin–spin relaxation time. In the absence of applied fields, the spin–spin relaxation time is approximately proportional to the square root of the reciprocal iron concentration. When external fields are applied, the dependence of the relaxation time on the concentration is considerably enhanced.

Mössbauer spectroscopy of FAS gives *in situ* information about the structure and composition of the different phases. This is supplementary to the information obtained by use of thermal analysis, which mainly concerns the phase transitions.

Contrary to several other systems,[15,21] the system studied here did not have the highest probability of glass formation in a narrow range around the eutectic composition. We found that at a given cooling rate glasses are easily formed when a certain critical salt concentration is exceeded. At lower salt concentrations, ice crystallizes during cooling, while the solution becomes more concentrated and finally solidifies into a glass. During exposure of these samples to a temperature above the glass temperature, irreversible changes take place. These changes may be explained in terms of the metastable phase diagram.

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